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Microstructure and superconductivity of MgB_2 single crystals

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Abstract

The hexagonal-disc-shaped MgB_2 single crystals were synthesized under the high-pressure conditions. The crystal symmetry, lattice constants as well as the Laue pattern of these single crystals were obtained from X-ray micro-diffraction. A crystallographic mapping showed that the edge and the *c*-axis of hexagonal-disc shape exactly matched the $[1\,0\,\bar{1}\,0]$ and $[0\,0\,0\,1]$ directions of the MgB_2 phase. This clearly confirmed that above well-shaped single crystals could be excellent samples to study the unsolved direction dependencies of the physical properties.

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Keywords: MgB_2; Impurity phase; X-ray micro-diffraction

1. Introduction

The recent discovery of MgB_2 [1] superconductor is quite interesting in science and in industrial application [2–6]. MgB_2 is characterized by an anisotropic, complex Fermi surface consisting of two bands: a 3D tubular network of mostly boron π-bands and 2D cylindrical sheets from boron σ-band [7]. Also experimentally observed tunnelling spectra [8,9], specific heat [10], magnetometry [11], transport [12], as well as penetration depth [13] are very much related to the two band nature. Other controversial issues such as anisotropic Hc2 [14,15], magnetoresistance, and residual resistivity ratio [16] could be solved only when high quality single crystals are available.

Here, we report the synthesis as well as X-ray micro-diffraction of high quality of MgB_2 single crystals. Surprisingly these are hexagonal-disc shapes with well defined shiny surfaces, which is quite different from the irregular shape MgB_2 single crystals synthesized in different conditions. In this sense, our single crystals are unique as far as the shape is concerned. The maximum length of diagonal and the thickness were about 250 and 20 μm, respectively. The crystallinity was identified from the Laue pattern using the X-ray micro-diffractometer in advanced light source (ALS). Both the edge and the *c*-axis of the hexagonally shape disc were found to match the crystal symmetry.

2. Experiments

The well ground mixtures of Mg and B powders were pressed into a pellet and placed in a Ta capsule. This capsule was put in a high-pressure cell with operating pressure of 3 GPa [17]. The heating temperature was around 1300–1500 °C. This temperature was maintained for about 30 min, and then was slowly cooled down to 800–900 °C. The polarizing optical microscope (POM) and a field-emission scanning electron microscope (FE-SEM) were used for the image of the crystal.

The average size of single crystals was about 50–100 μm if the sintering temperature was 1350 °C, but it became about 150–300 μm when the temperature increased to 1500 °C. The hexagonal shape of the single crystals is

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maintained if the size was less than 250 μm, but this was not the case of the larger crystals. Single crystals were carefully handled by using a homemade micro-tweezers. For the X-ray micro-diffraction measurements, several crystals were fixed at the center of Cu crosshairs on a substrate, as partially shown in Fig. 1(f). The Cu crosshairs were used for the purpose to facilitate the location of the sample by looking at the Cu fluorescence.

The instrument for X-ray micro-diffraction in the ALS is capable of producing a submicron-size X-ray micro-beam with submicron spatial resolution and thus can probe the local texture in a single crystal [18]. A high-purity Ge solid-state detector connected to a multichannel analyzer was used in this experiment. The crystal orientation can be determined with an accuracy of 0.01°.

3. Results and discussion

Fig. 1(a) shows POM image of MgB_2 single crystals. The edge angles of 120° and very flat, and shiny surfaces were well observed in this picture. The size of the crystal is about 70 μm in diagonal length and 10 μm in thickness respectively. The smooth surfaces and the sharp edges suggest that the probability of the mosaic aggregates of nanocrystals either along the *ab*-plane or along the *c*-axis in our crystals is very less. In this sense, it is better to study the intrinsic properties of MgB_2 using these single crystals. The single crystals reported so far, except us, had irregular shapes [19–21]. The largest single crystal of around 250 μm in diagonal length with sharp edge is shown in Fig. 1(b).

Fig. 1(c) shows a FE-SEM image of a MgB_2 single crystal with impurities which appeared as dislocation-type

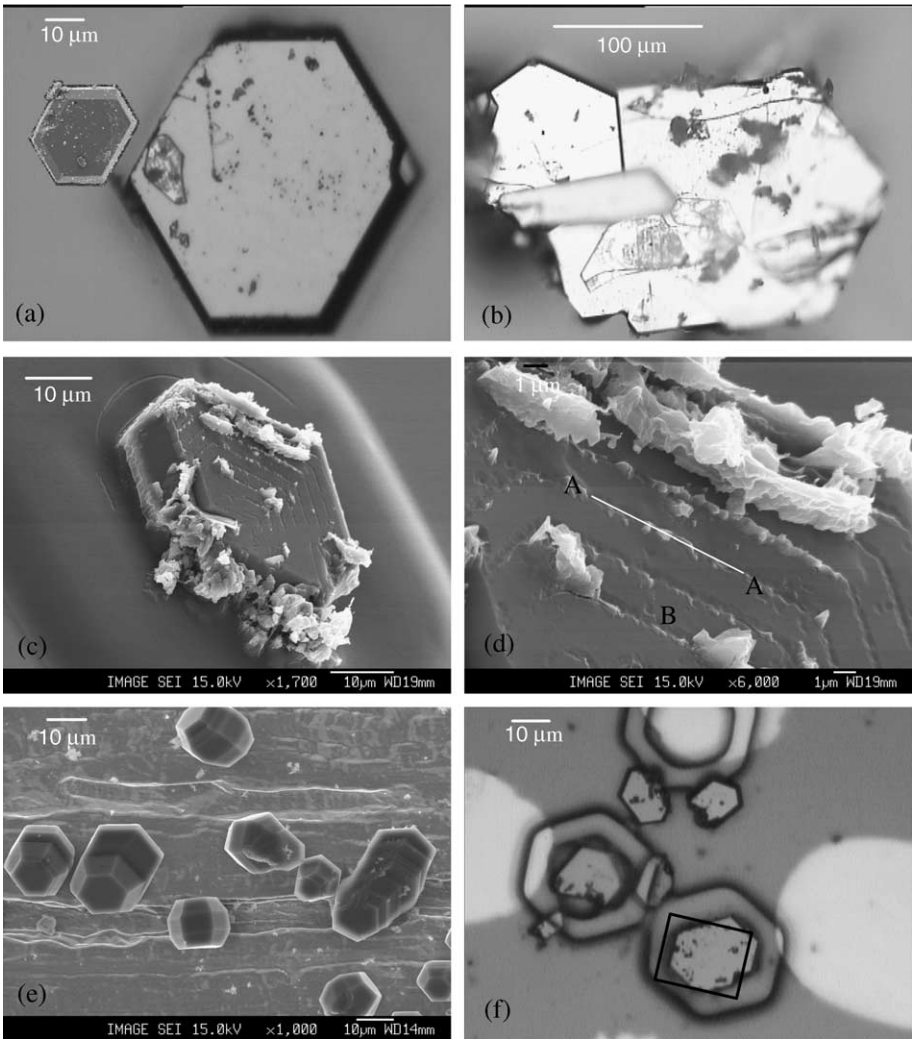

Fig. 1. Polarizing optical microscope and FE-SEM images of the MgB_2 single crystals. (a) MgB_2 single crystals with a diagonal distance of about 70 μm and with a thickness of about 10 μm respectively. (b) Biggest crystal with clear hexagonal edge. ((c), (d)) FE-SEM image of a single crystal with MgO impurities. (e) SEM images of Mg single crystals. (f) Polarizing optical microscope image of MgB_2 single crystals for a micro-XRD. An epoxy was used to fix six single crystals at the center of 100-μm-wide Cu crosshairs. The crystal enclosed by a rectangle was scanned for microstructural mapping in Fig. 2.

groove lines (like $\overline{AA}$ in (d) which is the zoom-in image of (c)). The groove lines are parallel to each other and have hexagonal traces. From the energy dispersive X-ray spectrometer (EDS) analysis, the groove lines are oxygen-rich phase and other regions (for example, the spot B) turned out to be pure MgB_2 phase. The groove lines do not meet each other, thus, are different from the spiral dislocation. As the time goes on, the groove region get swollen like the white scum at the edge shown in Fig. 1(d). The scum turned out to be MgO. The MgO phase may be produced during the synthesis and from the oxidation of Mg after synthesis. Fig. 1(e) is the SEM image of pure Mg single crystals which is verified by EDS and micro-XRD. Mg single crystal is regarded as a by-product of the Mg-rich MgB_2 synthesis. Mg crystal surface is composed of 2 hexagons and 6 rectangles and 12 trapezoids (total 20 surfaces). After 1 or 2 weeks in a normal desiccator, the silver-white luster disappears and turned to black. At the same time, etch pits appeared on the surface of Mg crystals by the oxygen and/or the moisture.

The crystal structure was identified by using white beam X-ray micro-diffraction measurements. For a micro-XRD, the MgB_2 single crystals are glued on the Si substrate shown in Fig. 1(f). The sample was positioned by 2 μm-step scanning. At each step, the Laue pattern (together with the Cu K fluorescence signal) was collected with a BRUKER 6000 CCD camera.

From the Laue pattern obtained from a MgB_2 single crystal, we can refine lattice parameters of $a = 3.0867 \pm 0.0003$, $c = 3.5235 \pm 0.0003$ Å and calculate the complete orientation matrix of the X-ray illuminated volume. The orientation variations inside the single crystal, in the right bottom corner of Fig. 1(f), are shown at Fig. 2(a) and (b). Here the deviations of angle from the mean values (6.0° and 26.0°, respectively) are represented. Fig. 2(a) is the out-of-plane orientation variation calculated as the angle between the c-axis and the normal to the surface of the silicon substrate. The gradual change from top to bottom of the crystal means that angle between the crystal c-axis and substrate c-axis changes from 6.2° to 5.8°, indicating a slight bending of the crystal. This assumption is also compatible with the fact that change of angle along the horizontal direction in the figure is much smaller. Another thing is that the crystal was put declined by 6° over Si substrate, which can result in bending of thin crystal during curing of epoxy existing between the crystal and the substrate. Thus, the real c-axis distribution seems to be quit lower than observed.

Fig. 2(b) shows the in-plane orientation variation calculated as the angle between the measured $[1\,0\,\bar{1}\,0]$ (hexagonal edge) direction and a reference direction (horizontal direction in the figure). The gradual change from top to bottom means that the angle changes from 26.2 to 25.8 °C. The average value of 26.0 °C is just the same as that of the angle between one of the crystal edges and the reference direction. The in-plane orientation also showed some inhomogeneities up to about 0.2°. Some small region in white or black showed a larger deviation of axes from other main region.

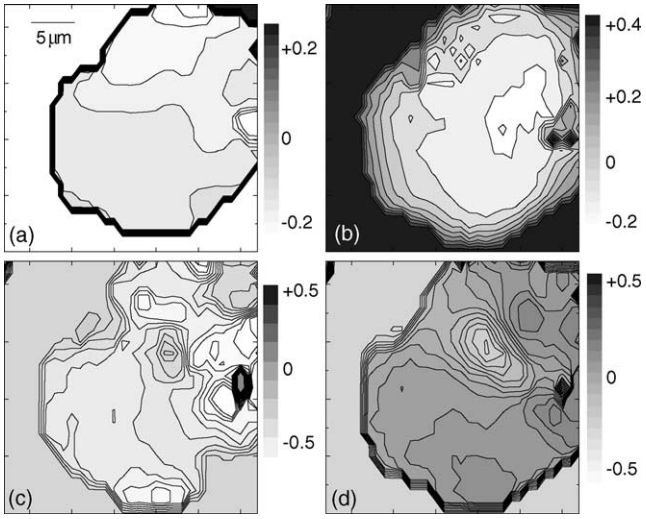

Fig. 2. (a) and (b) are, respectively, for the out-of-plane and the in-plane orientations inside a single crystal. Note that difference from mean values (6.0° and 26.0°, respectively) is shown in the vertical grey scale bars. The strains for $[1\,0\,\bar{1}\,0]$ and $[0\,0\,0\,1]$ direction are shown in (c) and (d) where vertical grey scale are in units of 10^{-3} in strain. The lateral scales are the same for all and scale bar of 5 μm is shown only in (a).

These mapping of orientation demonstrate that the orientation of crystal axis of our hexagonal-disc-shaped single crystals was perfect, within 0.2°. A recent study showed that $[0\,0\,0\,1]$ twist grain-boundaries, formed by rotations along the c-axis, typically by about 4°, were the major grain boundaries in polycrystalline MgB_2 [22]. This grain boundary was attributed to the weaker bonding between Mg layer and B layer. Note that bending observed in Fig. 2(a) could not give significant overestimation of in-plane axis distribution, and the real c-axis distribution seems to be lower than that observed in-plane axis distribution of the single crystal. This is also compatible with weak bonding between Mg layer and B layer.

The local strain mapping may also give information on the microstructure of the single crystal. For both the orientations, the regions with low strain are commonly observed near the center and peripheral region as shown in Fig. 2(c) and (d). The overall strain variations of about 6×10^{-4} across the crystal surface is quite low but higher than the resolution of about 10^{-4} and would correspond in variation of an unit on the last digit of lattice parameter. The average strain values were $\epsilon_{11} = 0.231 \times (1 \pm 0.141)10^{-3}$ and $\epsilon_{33} = -0.481 \times (1 \pm 0.154)10^{-3}$. The influence of lattice strain on the superconducting properties has been investigated also for polycrytalline MgB_2 [23]. The variations in lattice strain and Mg vacancy concentrations were obtained by

varying the synthesis conditions [24]. It was found that high strain (~1%) and the presence of Mg vacancies (~5%) resulted in lowering the T_c by only 2 K. Thus the strain of our crystals was more than 3 orders of magnitude smaller than that of polycrystals, which implies the strain or Mg vacancy may not account for the T_c difference between our single-crystal and polycrystals.

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